

CONTRIBUTION TO THE THEORY OF THE ADSORPTION EFFECT
AT THE SURFACE OF SEMICONDUCTORS AND GELS UNDER
THE ACTION OF IONIZING RADIATION

D.A.Aronov, Sh.A.Ablyayev, U.U.Pulatov, and R.G.Shamasov

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Discussion of the problem of determining the sign of the adsorption effect for semiconductors and gels as a function of the semiconductor (or gel) parameters and of the test temperature and pressure. A solution is obtained within the framework of the mechanism of electron chemisorption theory, for the case of strong absorption when ionizing radiation leads to the occurrence of electron-hole pairs near the surface.

At present, many experimental studies [e.g. (Bibl.1), Sect.10b] point out that radiation (illumination, gamma-quanta, high-energy charged particles) produces variations in the adsorption properties of semiconductors. In recent years, changes in adsorptivity under the influence of gamma-rays or irradiation with electrons have been observed in gels (Bibl.2, 3). An analysis of these findings indicates that the magnitude and polarity of the adsorption effect depend on the nature of the adsorbent and of the adsorbed substance, on the experimental conditions (pressure, temperature), surface state of the specimen (treatment), and its previous history. A change in the polarity of the effect can be obtained by treating the specimen with specific substances or by varying the ambient gas pressure or the surface condition.

Studies of the theory of this problem are relatively few. An attempt to

* Numbers in the margin indicate pagination in the original foreign text.

construct the theory of the photoadsorption effect in semiconductors was first made by F.F.Vol'kenshteyn et al. [(Bibl.4 - 6) and Sect.10a (Bibl.1)], based on the electron theory of chemisorption. Considering that the photoadsorption and cathodic adsorption effects have many aspects in common, this theory apparently can be extended to the cathodic adsorption effect in gels. In fact, gels are not perfect dielectrics and, given the presence of a sufficiently large amount of impurities, can be regarded as semiconductors with a wide forbidden zone (7 - 8 ev).

The difference between the effect of light and the effect of slow electrons with an energy of 10 - 12 ev lies chiefly in that, owing to strong absorption, electrons act mainly on the upper layer of a body, there causing relatively numerous structural perturbations and excited states, while negatively charging the gel surface. As in the case of illumination, this leads to a change in the concentration of free current carriers in the surface layer which, in its turn, may cause a change in the adsorptivity of the gel (Bibl.4, 6). The effect of volume on the observed effect consists chiefly in a part of the carriers generated by illumination or electron bombardment diffusing into the body and recombining there.

As in another case (Bibl.6), the aim of the present investigation was to determine - from the viewpoint of the mechanism of the electron theory of chemisorption - the polarity of the adsorption effect as a function of the parameters of the semiconductor (or gel) and of the experimental conditions, but based on premises that differ somewhat (Bibl.6). We will consider the case of strong absorption, in which ionizing radiation produces electron-hole pairs in the neighborhood of the surface. Because of the rapid attenuation of the electric /64 field from the surface toward the interior of the crystal, we will derive the

solution of the corresponding equations in the quasi-neutrality approximation. An arbitrary course of the potential is assumed in this solution; actually, however, this course is such that $\exp \left[\pm \frac{V_0(x)}{kT} \right]$ rapidly fluctuates with variations in $V_0(x)$. Hence, the solution does not require a linear approximation of the potential curve such as was applied by the above author (Bibl.6). Moreover, in contrast to the latter, in determining the carrier distributions, we will take the surface recombination into consideration.

It is known (Bibl.4 - 6) that the polarity of the adsorption effect is determined by the polarity of the parameter

$$\gamma = \frac{\Delta n_s}{\Delta p_s} \cdot \frac{n_{0s}}{p_{0s}} \exp \left(\frac{\epsilon_F - V_{0s} + v}{kT} \right) - 1, \quad (1)$$

where

n_{0s} and p_{0s} = electron concentrations in the conduction zone and hole concentrations in the valence zone, respectively, at the crystal surface in the absence of radiation;

Δn_s and Δp_s = radiation-induced additions to these concentrations;

ϵ_F = position of the Fermi level in the nonirradiated specimen, reckoned from the center of the forbidden zone (Fig.1);

V_{0s} = quantity characterizing the surface curvature of zones.

If the surface is negatively charged, the zones are curved upward ($V_{0s} > 0$);

v = position of the surface level A of the adsorbed particle.

For adsorption of acceptor particles, the polarity of the effect coincides with that of γ , while for adsorption of donor particles, it is reversed.

As before (Bibl.6), we will hereafter analyze in eq.(1) the dependence of the additions Δn_s and Δp_s on the rate of incident radiation and the magnitude

of ϵ_F and V_{0s} .

1. Calculation of the Carrier Distributions $\Delta n(x)$ and $\Delta p(x)$

Let us consider a general case where a crystal contains acceptor and donor impurities, with concentrations of N_A and N_D (Fig.1). Let us assume that the

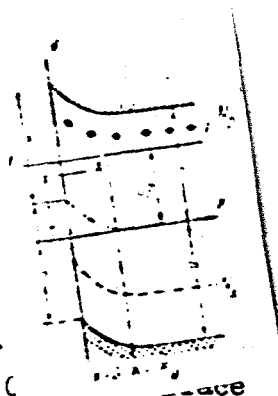


Fig.1 Energy Diagram of ... or Gel with Negatively (...)
 $0 \leq x \leq x_0$ = volume-charge region, $x \geq x_0$ = quasi-neutral region.

half-space $x \geq 0$ is occupied by a solid, while the region $x < 0$ represents a gaseous medium. Let us also assume that the surface $x = 0$ is illuminated by light or irradiated with slow electrons in the direction $x > 0$, where $g(x) = g_0$ at $x = 0$ and $g(x) = 0$ at $x > 0$ (g denotes the number of electron-hole pairs excited by irradiation per cm^2 of surface per unit time).

Given these assumptions, the behavior of electrons and holes during small-scale equilibrium perturbations is determined by the system of equations (Bibl.6)

$$\frac{dj_p}{dx} - \frac{dj_n}{dx} = -\frac{\Delta n}{\tau_n} - \frac{\Delta p}{\tau_p}, \quad (2)$$

$$j_n = -D_n \left(\frac{d\Delta n}{dx} + \Delta n \frac{eE_0}{kT} + n_0 \frac{e\Delta E}{kT} \right), \quad (3)$$

$$j_p = -D_p \left(\frac{d\Delta p}{dx} - \Delta p \frac{eE_0}{kT} - p_0 \frac{e\Delta E}{kT} \right), \quad (4)$$

$$\frac{d\Delta E}{dx} = \frac{4\pi e}{\epsilon} [(1 + \epsilon_p) \Delta p - (1 + \epsilon_n) \Delta n]. \quad (5)$$

Here,

j_n and j_p ($j_n = j_p$), n and p , D_n and D_p , τ_n and τ_p = flux, concentration,

diffusion coefficient, lifetime of electrons and holes, respectively;

$E = (1/e)(dV/dx)$ = intensity of the electric field;

V = potential energy of the electron;

e = absolute value of electron charge;

ϵ = dielectric constant of the crystal;

$N_D^+ = \delta_p \Delta p$ and $N_A^- = \delta_n \Delta n$ = concentrations of positively charged donors

and negatively charged acceptors, respectively.

The solution of eqs.(2) and (4) in the region of the volume charge $0 \leq x \leq x_0$, neglecting the recombination terms $\Delta n/\tau_n$ and $\Delta p/\tau_p$ by virtue of the assumption that a strong electric field exists at the crystal surface ($|\Delta E/E_0| \ll \Delta n/n_0, \Delta p/p_0$), will then be

$$\Delta n(x) = \Delta n_s \left(e^{\frac{V_{0s} - V_0(x)}{kT}} + \frac{s_n}{D_n} \int_0^x e^{\frac{V_0(x') - V_0(x)}{kT}} dx' \right) - \frac{K_0}{D_n} \int_0^x e^{\frac{V_0(x') - V_0(x)}{kT}} dx', \quad (6)$$

$$\Delta p(x) = \Delta p_s \left(e^{\frac{V_0(x) - V_{0s}}{kT}} + \frac{s_p}{D_p} \int_0^x e^{\frac{V_0(x) - V_0(x')}{kT}} dx' \right) - \frac{K_0}{D_p} \int_0^x e^{\frac{V_0(x) - V_0(x')}{kT}} dx'. \quad (7)$$

In deriving eqs.(6) and (7), we made use of the boundary conditions

$$\left. \begin{aligned} j_n = \text{const} = j_0 - s_n \Delta n_s &= -D_n \left(\frac{d\Delta n}{dx} + \frac{\Delta n}{kT} \cdot \frac{dV_0}{dx} \right) \\ j_p = \text{const} = j_0 - s_p \Delta p_s &= -D_p \left(\frac{d\Delta p}{dx} - \frac{\Delta p}{kT} \cdot \frac{dV_0}{dx} \right) \end{aligned} \right\} \quad (8)$$

Here, s_n and s_p are the surface recombination rates of electrons and holes, respectively.

The expressions $\Delta n(x_0)$ and $\Delta p(x_0)$ include the integrals $\int_0^{x_0} \exp \left[\pm \frac{V_0(x')}{kT} \right] dx'$ from eqs.(6) and (7), which can be accurately calculated only by numerical methods. Their approximate values, however, can be established on the basis of the following reasoning:

In the expression

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$$J = \int_0^{x_0} \exp \left[\frac{V_0(x')}{kT} \right] dx' = \int_{V_0}^0 \exp \left(\frac{V_0}{kT} \right) \left(\frac{dV_0}{dx} \right)^{-1} dV_0$$

the exponential function rapidly increases with increasing $V_0(x)$ and the major contribution to the integral is made by integration over the region where $V_0(x)$ is maximal, i.e., in the neighborhood of $x = 0$. Then, it is possible to derive from under the integral sign the value of $(dV_0/dx)^{-1}$ at that point and

$$J \approx \left(\frac{dV_0}{dx} \right)^{-1}_{x=0} \int_{V_0}^0 \exp \left(\frac{V_0}{kT} \right) dV_0 = \frac{kT}{eE_{0s}} \left(1 - e^{-\frac{V_{0s}}{kT}} \right).$$

Analogously,

$$\int_0^{x_0} \exp \left[-\frac{V_0(x')}{kT} \right] dx' \approx -\frac{kT}{eE_{0s}} \left(1 - e^{-\frac{V_{0s}}{kT}} \right).$$

Note that these relations are accurate in the particular case of a linear approximation of the curve of the potential $V_0(x) = eE_{0s} (x - x_0)$ employed elsewhere (Bibl.6).

In the region $x_0 \leq x \leq \infty$, where $n_0 = \text{const}$, $p_0 = \text{const}$, $E_0 \approx 0$, $V_0 \approx 0$, eqs.(2) - (5) are solved on the basis of the quasi-neutrality approximation, as opposed to the method used before (Bibl.6). According to this approximation, $dE/dx \approx 0$, and eq.(5) will yield

$$\Delta n = [(1 + \epsilon_p)(1 + \epsilon_n)] \Delta p. \quad (9)$$

Considering eq.(9), eqs.(2) - (5) will furnish, for $\Delta p(\infty) = 0$,

$$\Delta E = -\frac{kT}{e} \cdot \frac{[(1 + \epsilon_p)(1 + \epsilon_n)] D_n - D_p}{D_n n_0 + D_p p_0} \cdot \frac{d\Delta p}{dx}. \quad (10)$$

$$j_n = j_p = -D \frac{d\Delta p}{dx}. \quad (11)$$

$$\Delta p(x) = A \exp \left(-\frac{x}{L} \right). \quad (12)$$

where

$$D = \frac{D_p D_n \left(n_0 + \frac{1+b_p}{1+b_n} p_0 \right)}{D_n n_0 + D_p p_0} \quad (13)$$

$$L^2 = D \tau, \quad \frac{1}{\tau} = \frac{1}{\tau_p} + \frac{1+b_p}{1+b_n} \cdot \frac{1}{\tau_n} \quad (14)$$

The integration constants A and x_0 are eliminated with the aid of the conditions for "joining" the solutions of eqs. (9) and (6), (12) and (7), (19) and (8) at $x = x_0$. If, at the crystal surface, there exists a strong electric field ($E_{0s} \sim 10^3 - 10^5 \frac{V}{cm}$) such that

$$\left| \frac{1+b_n}{1+b_p} \cdot \frac{D}{D_p} \cdot \frac{kT}{eE_{0s}L} \left(1 - e^{-\frac{V_{0s}}{kT}} \right) \right| \ll 1 \quad (15)$$

then the expressions for Δn_s and Δp_s assume the form

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$$\Delta n_s = \frac{s_n^*}{L} \exp \left(-\frac{V_{0s}}{kT} \right) / \left(1 + \frac{s_n^* L}{D} \right) \quad (16)$$

$$\Delta p_s = \frac{s_p^*}{L} \exp \left(+\frac{V_{0s}}{kT} \right) / \left(1 + \frac{s_p^* L}{D} \right) \quad (17)$$

where $s_n^* = s_n \exp \left(-\frac{V_{0s}}{kT} \right)$ and $s_p^* = s_p \exp \left(+\frac{V_{0s}}{kT} \right)$ are the effective values of the electron - hole surface recombination rates, due to the fact that the current carriers do not recombine on a neutral surface but on a charged surface in whose neighborhood the zones show a marked curvature.

The total free-carrier concentration at the surface (concentration of free carriers generated by irradiation) is $\Delta n_s = \Delta n_s + \Delta p_s$. These free charges chiefly represent the new adsorption nuclei which appear at the surfaces of gels or semiconductors when these are exposed to slow electrons or strongly absorbable light. The number of gas molecules additionally adsorbed on the crystal surface after irradiation will clearly be proportional to the sum of the concentrations of free carriers and defects:

$$\gamma = R [(\Delta n_s + \Delta p_s) + N_s] \quad (18)$$

Here, R is the proportionality factor, and N_s is the concentration of surface defects.

2. Discussion of the Findings

Substituting eqs.(16) and (17) into eq.(1) and considering that, according to Karpenko (Bibl.6),

$$\left. \begin{aligned} n_{os} &= C_n \exp [-(u - \varepsilon_F + V_{os})/kT] \\ p_{os} &= C_p \exp [-(u + \varepsilon_F - V_{os})/kT] \end{aligned} \right\} \quad (19)$$

we can determine γ (assuming $C_n = C_p$):

$$\gamma = \exp(-\varphi^*/kT), \quad (20)$$

where

$$\varphi^* = \varphi - kT \ln \left[\frac{1 + \frac{s_p L}{D} \exp(V_{os}/kT)}{1 + \frac{s_n L}{D} \exp(-V_{os}/kT)} \right], \quad (21)$$

$$\varphi = \varepsilon_F + V_{os} - \psi. \quad (22)$$

Here, it is assumed that $\delta_p \approx \delta_n$ (case of nearly total compensation of impurities) or $\delta_p = 0$, $\delta_n \ll 1$ (case of p-type semiconductor), $\delta_n = 0$, $\delta_p \ll 1$ (case of n-type semiconductor).

From eqs.(20) and (22) it can be seen that the polarity of γ and hence also the polarity of the adsorption effect is determined not just by the polarity of ψ (Bibl.6) but also by the ratios of the effective surface recombination rates of electrons and holes to their recombination within the volume of the semiconductor, i.e., in the final analysis by the polarity of ψ^* .

Let us consider particular cases, by means of which the role of surface and volume recombinations can be defined.

1. The volume recombination rate $\frac{D}{L}$ of carriers greatly exceeds the surface recombination rates, i.e., /68

$$\frac{D}{L} \gg s_p \exp(V_{os}/kT), \quad -\frac{D}{L} \gg s_n \exp(-V_{os}/kT). \quad (23)$$

Under these conditions φ^* differs little from φ so that the formula for γ derived by Karpenko (Bibl.6) is obtained. In this case, the criterion of the

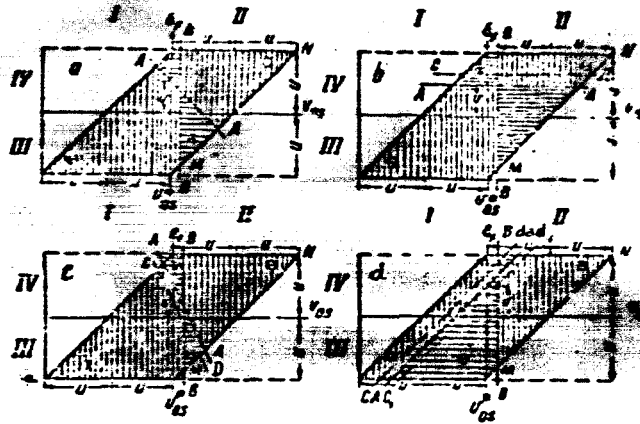


Fig.2 Diagrams of Adsorption Effect for Gels and Semiconductors
Exposed to Ionizing Radiation

The "plus" sign corresponds to adsorption and the
"minus" sign, to desorption:

- I - Surface charged positively (zones curved downward), donor particles adsorbed; II - Surface charged negatively (zones curved upward), acceptor particles adsorbed; III - p-type semiconductors; IV - n-type semiconductors.

polarity of the adsorption effect is in agreement with Karpenko's criterion (Bibl.6) according to which the polarity of the effect, in the presence of a specified v , is determined solely by the position of the Fermi level in the crystal and the degree of surface curvature of the zones (diagram in Fig.2a). In the diagram, the lines AA and BB cut the entire region of adsorption into sectors of positive and negative effects, which are correspondingly designated. The displacement of the Fermi level ϵ_f (at $V_{0s} = \text{const}$) or any change in the degree of curvature of the zones V_{0s} (at $\epsilon_f = \text{const}$) as well as in both these parameters simultaneously, may lead to a reversal in polarity of the effect. Equations (20) - (22), on the other hand, imply that the polarity of the effect

is influenced not only by the work function (V_0) or by the electric conductivity of the crystal (ϵ_f) but also by the variations in the ratio of the volume to surface recombination rates of the carriers.

2. The crystal surface is so treated that the surface recombination rate of holes is high and that of electrons low, compared with the volume recombination rate, i.e.,

$$\frac{D}{L} \ll s_p \exp(V_{0s}/kT), \frac{D}{L} \gg s_n \exp(-V_{0s}/kT). \quad (24)$$

In this case, eqs.(21) and (20) will yield

$$\left. \begin{aligned} \varphi^* &\approx \epsilon_f - v - kT \ln(s_p L/D) \\ \gamma &\approx (s_p L/D) \exp[-(\epsilon_f - v)/kT] - 1 \end{aligned} \right\}. \quad (25)$$

i.e., the polarity of the effect is independent of the surface curvature of the zones; it is positive if

$$s_n > \frac{D}{L} \exp\left(\frac{\epsilon_f - v}{kT}\right). \quad (26)$$

and negative if the sign in the inequality (26) is reversed. It is characteristic that the polarity reversal of γ is independent of V_0 , and the polarity of the effect, at given v , is highly reactive to changes in ϵ_f and weakly reactive to the quantity $s_p/\frac{D}{L}$ and thus is entirely determined by the displacement of the Fermi level (Fig.2b). The sectors of positive and negative effects are separated by mutually perpendicular lines AA and BB; the sector of positive effect expands because of the predominance of surface over volume recombination, to the extent indicated by the broken line CD.

3. The surface of the body is so treated as to satisfy inequalities opposite to inequality (23), i.e.,

$$\frac{D}{L} \gg s_p \exp(V_{0s}/kT), \frac{D}{L} \ll s_n \exp(-V_{0s}/kT). \quad (27)$$

In this case, eqs.(21) and (20) give

$$\left. \begin{aligned} \varphi^* &\approx z_p - v + 2V_{os} + kT \ln (s_p L/D) \\ \tau &= (D/s_n L) \exp \left[- (z_p - v + 2V_{os}) / kT \right] \end{aligned} \right\} \quad (28)$$

meaning that the polarity of γ is strongly influenced by the curvature of the zones and that (at $V_{os} > 0$), because of eqs.(27), the variation range in the polarity of the effect on variations in the crystal parameters, temperature, surface state, and position of the level of the adsorbed particle, will be extremely narrow. For this case, $\gamma < 0$ is characteristic, i.e., desorption of acceptor and adsorption of donor particles are involved here (Fig.2c). The presence of a marked surface recombination restricts the range of adsorption of acceptor particles and broadens the range of adsorption of donor particles (broken line CD in Fig.2c).

4. The volume recombination of carriers is very low, so that

$$\frac{D}{L} \ll s_p \exp (V_{os}/kT), \quad \frac{D}{L} \ll s_n \exp (-V_{os}/kT) \quad (29)$$

From eqs.(21) and (20) it follows that

$$\left. \begin{aligned} \varphi^* &\approx z_p - V_{os} - v - kT \ln (s_p/s_n) \\ \tau &\approx (s_p/s_n) \exp \left[- (z_p - V_{os} - v) / kT \right] - 1 \end{aligned} \right\} \quad (30)$$

Equation (30) differs from the corresponding formulas by Karpenko (Bibl.6) only by the sign of V_{os} . This is also evident from a comparison of the diagrams in Figs.2d and 2a; the line AA runs parallel to the line MN rather than at right angles thereto as in Fig.2a. The sector with $\gamma > 0$ is sufficiently broad, which essentially differs from the case considered by Karpenko (Bibl.6). Depending on which of the two surface recombination rates of carriers is higher, the regions of positive and negative effects may either broaden or contract (line AA in Fig.2d is shifted parallel to itself and occupies the position of the lines CD or C_1D_1).

Note that in Fig.2 the regions with positive and negative γ may contract

and expand also owing to variations in V_0^* due to surface states of nonadsorptive origin ($V_0^* \geq 0$). Then, the line BB will be displaced to the left or right /70 parallel to itself.

An analysis of eqs.(20) - (22) and Fig.2 demonstrates that, from the viewpoint of adsorptive properties, the most favorable cases are those described by eqs.(24) - (25) and (29) - (30) if the volume recombination of carriers is sufficiently low compared with their surface recombination. It is conceivable that such conditions are satisfied in gels, which have a strongly developed surface; in such gels, by virtue of the above factors, adsorption effects reach a particularly high value, as experimentally observed by Starodubtsev et al. (Bibl.7-9) on irradiating gels with fluxes of slow electrons.

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Physico-Technical Institute

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